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Synthetic Methods

Catalytic Asymmetric β,γ Activation of α,β-Unsaturated γ-Butyrolactams: Direct Approach to β,γ-Functionalized Dihydropyranopyrrolidin-2-ones**

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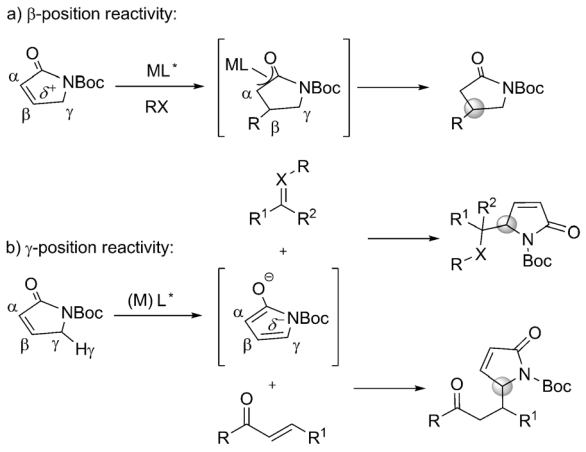
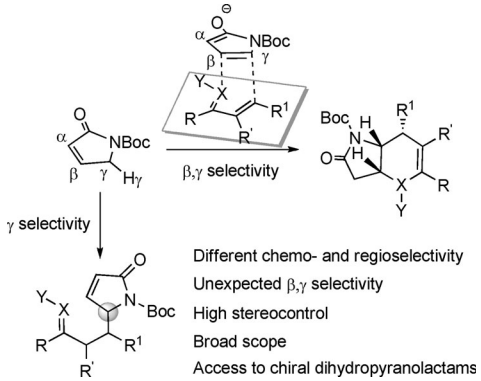
The divergence of natural products resulting from evolution provides organic chemists with a prodigious starting point to design and construct a diverse array of bioactive compounds having select, naturally occurring core scaffolds.[1] Chiral pyrrolidin-2-ones have been found as key structural elements commonly appearing in a series of biological assays.[2] As a direct precursor to pyrrolidin-2-one derivatives, α,β-unsaturated γ-butyrolactams recently emerged as the most attractive reactants in asymmetric organometallic or organocatalytic reactions for the synthesis of chiral β- and γ-functionalized pyrrolidin-2-ones (Scheme 1). For example, elegant work involving the asymmetric organometal-catalyzed 1,4-additions to introducing C4 chirality at the β position (Scheme 1 a),[3] and the selective functionalization of the γ position through asymmetric vinylogous aldol,[4] Mannich,[5] and Michael[6] reactions have been developed (Scheme 1 b). Although these efficient catalytic asymmetric methods have been well-established for the either the β or γ position of α,β-unsaturated γ-butyrolactams, to date, the direct catalytic dual activation of both the β and γ positions remains unknown. If this dual activation can be achieved, it will contribute to the development new catalytic asymmetric reaction modes, thereby providing a new synthetic methodology to enantioselectively construct more versatile β,γ-functionalized pyrrolidinone architectures. For these reasons, we present herein our preliminary results on this topic.



Scheme 1. Different reactive position of α,β-unsaturated γ-butyrolactams in catalytic asymmetric reactions. Boc = *tert*-butoxycarbonyl.

Inspired by the utilization of in situ generation of enolates,[7] we postulated that the selective β,γ activation of α,β-unsaturated γ-butyrolactams through the in situ formation of a 1,4-unsaturated enolate so as to raise the energy of the HOMO would be more feasible. In light of our recent studies on dual $HOMO_{dienophile}/LUMO_{diene}$-controlled asymmetric Diels–Alder (DA) reactions,[8] we rationalized that such activated 1,4-unsaturated enolates might serve as electron-rich dienophiles with a properly designed electron-deficient diene to undergo a β,γ-selective inverse-electron-demand DA [4+2] annulation, while avoiding the direct γ-selective vinylogous addition reaction as outlined in Scheme 2.



Scheme 2. Different chemo- and regioselectivity for catalytic reactions of α,β-unsaturated γ-butyrolactams with enones.

The catalytic asymmetric inverse-electron-demand DA [4+2] annulation has been widely recognized as one of the most powerful and convergent strategies for construction of stereochemically dense cyclohexenyl rings,[9] and has been partly addressed in elegant work involving the activation of dienes through a LUMO-lowering strategy with the aid of

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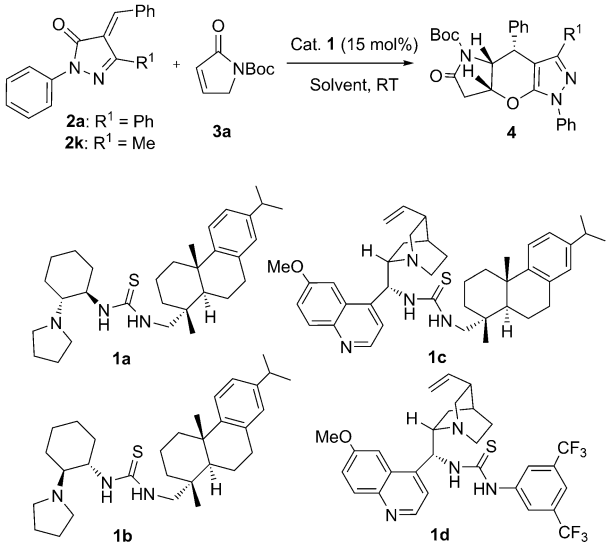
Lewis-acidic metal complexes[10] or organic molecules,[11] as well as an enamine catalytic approach involving the HOMO of electron-rich dienophiles described by the groups of Jørgensen[12] and Chen.[13] However, we realized that all catalytic reactions of α,β-unsaturated γ-butyrolactams with unsaturated carbonyls exclusively fall into the category of only γ-selective asymmetric processes as reported.[6] In contrast, the single LUMO or HOMO activation approach cannot provide sufficient capacity to initiate the dual activation of both the β,γ positions of unsaturated γ-butyrolactams. Alternatively, our laboratory recently developed a bifunctional catalytic system involving dual control of $HOMO_{dienophile}$ and $LUMO_{diene}$ activation.[8] We surmised that this bifunctional strategy could serve as a platform for catalyzing the asymmetric IEDDA of α,β-unsaturated γ-butyrolactams with unsaturated pyrazolones in a direct β,γ-activation fashion. Herein, we report the successful execution of this reaction. Moreover, this catalytic approach allows the formation of a diverse range of β,γ-functionalized dihydropyranopyrrolidin-2-one architectures in only one step.

To begin our initial investigation, several bifunctional organocatalysts[14] were firstly screened to evaluate their ability to promote the β,γ-selective IEDDA reaction of the α,β-unsaturated γ-butyrolactam **3a** with the unsaturated pyrazolone **2k** in the presence of 15 mol% of the catalyst at room temperature in CH_2Cl_2 (entries 1–4, Table 1). These results indicated that the thiourea catalyst **1c** is the best catalyst in terms of chemical yield and enantioselectivity, thus furnishing the products with excellent diastereoselectivity in 48% yield and 50% *ee* (entry 3). Subsequently, a survey of other solvents was carried out with the catalyst **1c** (entries 5–9). We found that a change in the solvent has a significant effect on the reaction. Among the solvents tested, diethyl ether appeared to be the most suitable reaction media, thus giving the product with 83% *ee* (entry 6). To our delight, a higher yield and enantioselectivity (62% yield, and 92% *ee*) can be observed in the presence of 30 mol% of benzoic acid (entry 8). In addition, It is worth noting that the catalyst **1b** could catalyze the reaction to give the desired product with high yield, enantioselectivity, and diastereoselectivity when the C3 phenyl-substituted unsaturated pyrazolone **2a** was employed in CH_2Cl_2 (entry 12). These results suggested that the C3 substituent of the unsaturated pyrazolone has a strong influence on the activity of the reaction. Compared to alkyl-substituted substrates, the aryl-substituted pyrazolone prefers the less polar solvent and smaller sterically hindered thiourea catalyst for higher stereoselectivity and yield.

The results of experiments run under the optimized reaction conditions to probe the scope of the reaction are summarized in Table 2. The catalytic β,γ-selective IEDDA reaction of α,β-unsaturated γ-butyrolactams with C3 phenyl-substituted unsaturated pyrazolones in the presence of 15 mol% of **1b** were performed. A variety of C3 phenyl-substituted unsaturated pyrazolones, including those bearing electron-withdrawing and electron-donating substituents on the aryl ring, as well as heterocycles, was examined. Gratifyingly, all of the reactions provided excellent diastereoselectivity. In general, the results showed that, except for the 2-thienyl-substituted unsaturated pyrazolones (entry 10), all

Table 1: Studies and optimization of the reaction parameters.[a]



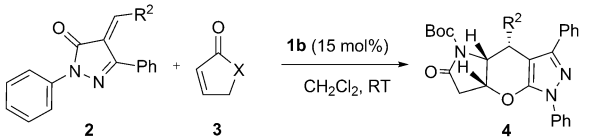
Entry	Cat.	R^1	Solvent	Yield [%][b]	*ee* [%][c]
1	**1a**	Me	CH_2Cl_2	42	−20
2	**1b**	Me	CH_2Cl_2	50	30
3	**1c**	Me	CH_2Cl_2	48	50
4	**1d**	Me	CH_2Cl_2	38	25
5	**1c**	Me	THF	35	40
6	**1c**	Me	Et_2O	52	83
7	**1c**	Me	toluene	trace	n.d
8[e]	**1c**	Me	Et_2O	62	92
9[f]	**1c**	Me	Et_2O	48	80
10	**1c**	Ph	Et_2O	67	61
11	**1b**	Ph	Et_2O	71	63
12[d]	**1b**	Ph	CH_2Cl_2	85	90

[a] Unless noted otherwise the reaction was conducted with **2** (0.11 mmol) and **3a** (0.10 mmol) for 72 h at room temperature. [b] Yield of isolated product. Products were observed with >20:1 d.r. [c] The *ee* values were determined by HPLC, and the configuration was assigned by comparison of HPLC data and X-ray crystal data of **7b**. The d.r. values were determined by ^{1}H NMR spectroscopy and HPLC. [d] 48 h. [e] Using a 30 mol% benzoic acid. [f] Using a 30 mol% AcOH.

reactions with aromatic, unsaturated pyrazolones proceeded cleanly, thus affording the desired products in excellent enantioselectivities with good to high yields (entries 1–9). It is worth noting that the lactone **3b** proved to be essentially inactive for this DA [4+2] annulation (entry 11).

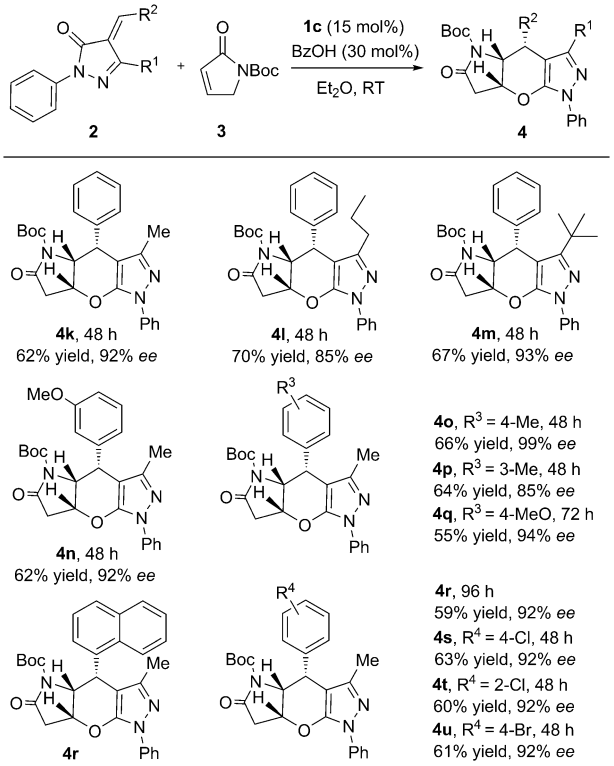
With the successful synthesis of various β,γ-functionalized dihydropyranopyrrolidin-2-ones using C3 phenyl-substituted unsaturated pyrazolones, as described above, other diversely substituted unsaturated pyrazolones were tested under the **1c**-catalyzed asymmetric protocol (Scheme 3). The results showed that various aliphatic groups at C3 of the unsaturated pyrazolones could be tolerated, and gave the diversely structured corresponding compounds **4k**–**u** with high to excellent enantioselectivities (85–99% *ee*) and diastereoselectivities (>20:1 d.r.) in yields ranging from 55% to 70%. The relative and absolute configurations of the products were determined by X-ray crystal structure analysis of **7b** (see the Supporting Information).

Table 2: Scope of substrates for asymmetric IEDDA reaction of γ-butyrolactam.[a]



Entry	R^2	Yield [%][b]	*cis*/*trans*[c]	*ee* [%][d]
1	Ph	85 (**4a**)	>20:1	90
2	4-FC_6H_4	90 (**4b**)	>20:1	93
3	4-ClC_6H_4	88 (**4c**)	>20:1	95
4	2-BrC_6H_4	75 (**4d**)	>20:1	90
5	3-BrC_6H_4	80 (**4e**)	>20:1	92
6	4-MeC_6H_4	83 (**4f**)	>20:1	94
7	3,4-$(CH_3)_2C_6H_3$	69 (**4g**)	>20:1	90
8	4-$MeOC_6H_4$	80(**4h**)	>20:1	95
9	3-$MeOC_6H_4$	83 (**4i**)	>20:1	94
10	2-thienyl	73 (**4j**)	>20:1	56
11[e]	Ph	<5	n.d.	n.d.

[a] Unless noted otherwise the reaction was conducted with **2** (0.11 mmol) and **3a** (0.10 mmol) for 48 h at room temperature. [b] Yield of isolated product. [c] Determined by ^{1}H NMR spectroscopy and HPLC. [d] The *ee* values were determined by HPLC, and the configuration was assigned by comparison of HPLC data and X-ray crystal data of **7b**. [e] The reaction was conducted with **3b** (0.10 mmol) for 48 h at room temperature.



Scheme 3. Synthesis of diversely structured bridged bicyclic dihydropyranolactams by using the established reaction conditions. Unless noted otherwise the reported yields are those of the isolated products and the *ee* values were determined by HPLC analysis. Bz = benzoyl.

To gain a better understanding of the scope of this conceptually new catalytic system, we hoped to expand substrates to *N*-tosyl-2-methylenebut-3-enoates.[15] A range of substituted *N*-tosyl-2-methylenebut-3-enoates was examined with α,β-unsaturated γ-butyrolactams in the catalytic β,γ-selective [4+2] annulation. Both electron-donating and electron-withdrawing substituents at different positions on the aromatic ring afforded the products in excellent diastereoselectivities and high to excellent enantioselectivities (entries 1–7, Table 3); even the electron-withdrawing substituent at the *meta* position provided a moderate product yield (entry 2). As expected, heterocyclic *N*-tosyl-2-methylenebut-3-enoates have also proven to be suitable substrates for this asymmetric process, thus furnishing the β,γ-functionalized bridged bicyclic dihydropyranopyrrolidin-2-ones **6h**,**i** and **6k**,**l** in high to excellent yields and enantioselectivities (entries 8 and 9 and 11–12). Additionally, when the COOMe on the *N*-tosyl-2-methylenebut-3-enoates was replaced by COOEt the reaction still proceeded smoothly, and the dihydropyranopyrrolidin-2-ones **6j–l** were also favorably formed in high yields with 90–93% *ee* (entries 10–12). The absolute and relative configurations of the bicyclic dihydropyranopyrrolidin-2-ones were unambiguously determined by X-ray crystallography (**6a**; see the Supporting Information).

On the basis of the experimental results described above and recent studies,[8a] we have proposed a possible transition-state model to explain the stereochemistry of the β,γ-selective IEDDA reaction of α,β-unsaturated γ-butyrolactams (Figure 1). The β,γ positions of α,β-unsaturated γ-butyrolactams could be activated (raising of the HOMO energy) simultaneously by in situ formation of a 1,4-unsaturated enolate through the tertiary amine moiety of the catalyst, while the unsaturated pyrazolone was activated (lowering of the LUMO energy) by the two thiourea hydrogen atoms through weak hydrogen bonds. As a result of the main stereochemical control from the dehydroabietic amine moiety of the thiourea,[16] high Re face and *endo*-β,γ selectivity would be enforced to give the desired chiral product, which is consistent with the experimental results.

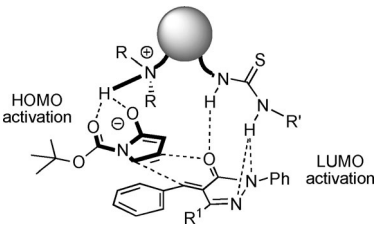
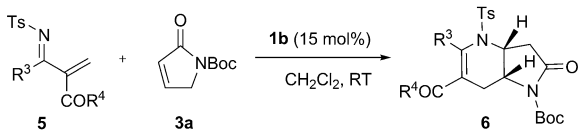
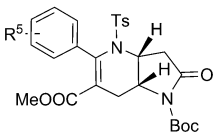
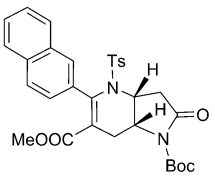
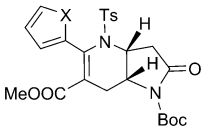
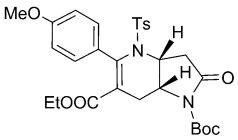
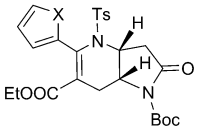


Figure 1. Proposed transition state for the reaction.

As an illustration in Scheme 4, the chiral products could be converted smoothly into the N-deprotected bridged tricyclic dihydropyranolactams by deprotection with trifluoroacetic acid in a simple step. As expected, several representative β,γ-functionalized dihydropyranopyrrolidin-2-ones (**7a–d**) were formed with good to high yield and enantioselectivities (72–90% yield, and 89–94% *ee*).

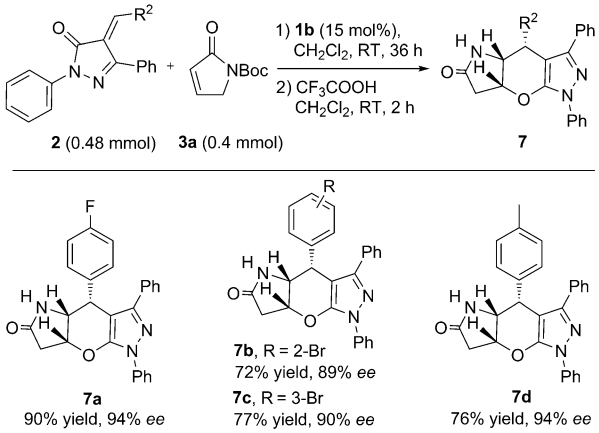
Table 3: Bridged bicyclic dihydropyranolactams formed by employing *N*-tosyl-2-methylenebut-3-enoates.[a]



Entry	Product	Yield [%][b]	*ee* [%][c]
			
1	R = H	86 (**6a**)	96
2[d]	R = 3-Cl	63 (**6b**)	85
3	R = 4-Me	95 (**6c**)	95
4	R = 4-MeO	98 (**6d**)	99
5	R = 3-Me	98 (**6e**)	97
6	R = 3,4-diMe	95 (**6f**)	99
			
7		96 (**6g**)	90
			
8		97 (X = O, **6h**)	97
9		91 (X = S, **6i**)	93
			
10		86 (**6j**)	90
			
11		85 (X = O, **6k**)	93
12		85 (X = S, **6l**)	90

[a] Unless noted otherwise the reaction was conducted with **5** (0.11 mmol) and **3a** (0.10 mmol) in toluene for 48 h at room temperature. [b] Yield of the isolated product. [c] The *ee* values were determined by HPLC, and except for **6b** = 8:1 d.r. and **6k** = 15:1 d.r., other products were observed with a > 20:1 d.r. value as determined by ^{1}H NMR spectroscopy and HPLC. Configuration was assigned by comparison of HPLC data and X-ray crystal data of **6a**. [d] For 96 h. Ts = 4-toluenesulfonyl.

In summary, we have disclosed a highly efficient strategy for the β,γ-selective activation of α,β-unsaturated γ-butyrolactams and it has enabled the development of the first catalytic β,γ-selective DA [4+2] annulation of α,β-unsaturated γ-butyrolactams. Furthermore, this process provides a direct method for the enantioselective construction of β,γ-functionalized bridged bi- or tricyclic dihydropyranopyrrolidin-2-one skeletons in only one step (up to 98% yield, > 20:1 d.r., and 99% *ee*).



Scheme 4. Synthetic deprotection of the chiral dihydropyranolactams.

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